

**Aqueous binders**Field of the Invention

5 The invention relates to aqueous binders. It further relates to a method of use of such binders in formulating baking enamels which even at comparatively low baking temperatures produce surfacers for automotive finishing which yield coatings with good stonechip resistance.

10 Background of the Invention

There is already patent literature describing binders for automotive surfacer materials which are distinguished by high stonechip resistance:

15 Thus, in DE-A 4142816 (corresponding to US-A 5,521,247) there is described an aqueous coating material comprising a reaction product of an acid-functional urethane resin and a hydroxyl-containing polyester resin in a mixture with a non-water-dilutable blocked polyisocyanate and an  
20 amine resin as a further crosslinker.

AT-B 408 657 (corresponding to US-A 6,521,700) relates to a condensation product of a carboxyl-containing resin and a hydroxyl-containing resin in combination with a curing  
25 agent composed of a mixture of a water-insoluble blocked isocyanate and a hydrophilically modified isocyanate.

In AT-B 408 658 (corresponding to US-A 6,406,753), a combination of the abovementioned condensation product is  
30 described with a curing agent comprising a water-insoluble nonblocked isocyanate and a hydrophilic, partly etherified amino resin.

35 In AT-B 408 659 (corresponding to US-A 6,423,771), the addition of a water-insoluble, low molar mass polyester,

rich in hydroxyl groups, to the abovementioned condensation products is disclosed.

EP-A 1 199 342 (corresponding to US 2002/0077389),  
5 finally, relates to particular, water-dilutable hydroxyurethanes as admixture resins, producing a distinct increase in the mass fraction of solids both of the binder supply form and of the coating material. In that case it was found, surprisingly, that such admixture 10 resins also improve the stonechip resistance.

All of the abovementioned systems, however, are in need of further improvement. For instance, the ever-increasing requirements of the automotive industry are not always 15 met with the stated systems. One particular recent requirement which has been added is the lowering of the baking temperature from its present level of about 160 to 170 °C to around 140 °C, with an underbake safety level down to about 130 °C, with no change in the high quality 20 of the cured coatings.

Summary of the Invention

It has now been found that, through addition of hydroxyurethanes **C** which can be prepared by reacting 25 flexible, "soft" polyfunctional hydroxy compounds **Ca** with rigid, "hard" polyfunctional isocyanates **Cb** to condensation products **AB** of hydroxyl-containing resins **B** and acid-functional resins **A** and through combinations of these mixtures with curing agents **D** which are effective 30 even at such low baking temperatures (130 to 140 °C) it is possible to obtain binders which on baking even in the temperature range from 130 to 140 °C lead to coatings which in addition to good all-round properties have excellent stonechip resistance.

The invention accordingly provides aqueous binders comprising condensation products **AB** of acid-functional resins **A** and hydroxyl-containing resins **B**, hydroxyurethanes **C**, and curing agents **D** which are active even at temperatures starting at 120 °C wherein the hydroxyurethanes **C** include units derived from polyfunctional hydroxy compounds **Ca** having at least 4 carbon atoms, it being possible for some of the carbon atoms to be replaced by oxygen atoms (in the form of ether bonds) or by ester groups, and at least two hydroxyl groups, which are preferably terminal, based on the longest chain of the molecule, and units derived from polyfunctional isocyanates **Cb** selected from isocyanates of the formula  $R(NCO)_n$ , where  $R$  is an  $n$ -functional cycloaliphatic, aliphatic-polycyclic, aromatic-aliphatic-branched or aromatic radical and  $n$  is at least 2.

Detailed Description of the Preferred Embodiments

By flexible or "soft" are meant hydroxy compounds **Ca** which contain an aliphatic chain having at least 4, preferably at least 5, and in particular at least 6 carbon atoms, it being possible where appropriate for some of the carbon atoms to be replaced by oxygen atoms or ester groups, with any branches present being excluded from the calculation. Preference is given to dihydroxy compounds. This definition covers, for example, 1,4-butanediol, 1,6-hexanediol, and higher homologs, diethylene glycol, triethylene glycol, and higher oligomers, dipropylene glycol, tripropylene glycol, and higher oligomers, and polycaprolactonediols as available, for example, from Interorganica in the ®Placel L series. Mixtures of these hydroxy compounds can also be used.

By rigid or "hard" are meant polyfunctional isocyanates **Cb** of the formula  $R(NCO)_n$  wherein the radical  $R$  is a cycloaliphatic, aliphatic-polycyclic, aromatic-aliphatic-

branched or aromatic radical, in the latter case the isocyanate groups preferably being attached to different aromatic nuclei. Preference is given to diisocyanates (n=2). This group includes, for example, isophorone  
5 diisocyanate, norbornane diisocyanate, dicyclohexylmethane diisocyanate, tetramethylxylylene diisocyanate, diphenylmethane diisocyanate, 4,4'-diisocyanatobiphenyl, and naphthalene 1,5-diisocyanate. Mixtures of these isocyanates can also be used.

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The hydroxyurethanes **C** are preferably of strictly linear construction - this is the case when exclusive use is made of diols as component **Ca** and of diisocyanates as component **Cb**. In order to achieve a certain degree of branching, which may be advantageous where appropriate, it is possible as well to use fractions (in each case up to 10 % of the difunctional reactants) of polyols, preferably triols, **Ca'** as part of component **Ca** and/or isocyanates **Cb'** having more than two isocyanate groups per molecule as part of component **Cb**. These substances of higher functionality are then no longer required to satisfy the aforementioned "hard/soft" definition. From the plethora of suitable polyols **Ca'** mention may be made, for example, of trimethylolpropane, trimethylolethane,  
25 ditrimethylolpropane, erythritol, pentaerythritol, sorbitol, and polycaprolactonetriols (@Placcel 300 series, Interorganica). Examples of suitable isocyanates **Cb'** having a functionality of more than 2 include trimerized hexamethylene diisocyanate (@Desmodur N 3300, Bayer, about 3 NCO groups per molecule) and oligomeric diphenylmethane diisocyanate with about 2.3 NCO groups per molecule (@Desmodur VL, Bayer).

35 The presence of hydroxyl groups in the hydroxyurethane **C** is ascertained by making sure that the amount of substance of the hydroxyl groups of component **Ca** is

always greater than that of the isocyanate groups of component **Cb** in the reactant mixture.

For the synthesis of the hydroxyurethanes **C** a preferred procedure is to introduce the hydroxy compound **Ca** or a mixture of hydroxy compounds **Ca** and to run the polyfunctional isocyanate **Cb** or a mixture of polyfunctional isocyanates **Cb** into this initial charge with stirring at from 50 to 130 °C at a rate such that the heat given off remains readily manageable. When addition is complete the reaction mixture is held at elevated temperature until no isocyanate groups, or virtually none, are detectable any longer.

For further processing the hydroxyurethanes **C** thus prepared can be used either in solvent-free form, as a melt, or else in dilution in an appropriate solvent, as admixture resins. Since these admixture resins are of only limited water-solubility, if any, the preparation of water-dilutable binders they must be "borne" by the water-soluble condensate formed from hydroxyl-containing and carboxyl-containing resins (see documents AT-B 408 657 and AT-B 408 658), in other words must be emulsified by these resins in water.

Through an appropriate choice of the stoichiometric proportions of the reactants **Ca** and **Cb** and of their functionality, where reactants with a functionality of more than two are used, it is possible to influence the degree of polymerization of the hydroxyurethane. It is preferred to aim for a range which produces a Staudinger index (formerly termed "intrinsic viscosity number") of at least 4 to a maximum of 25 cm<sup>3</sup>/g. The choice of the most favorable degree of polymerization in any given case depends on the one hand on compatibility with the particular condensate used and hence on the stability of

the binder dispersion, and on the other hand, of course, on the technical coating properties obtained (ease of application, surface quality, etc.). The most favorable degree of polymerization of the hydroxyurethane must be  
5 evaluated on a case-by-case basis. The hydroxyurethanes **C** preferably have a Staudinger index from 4 to 19 cm<sup>3</sup>/g, measured in dimethylformamide solvent at 23 °C.

The ready-made, water-soluble binders contain not only  
10 said hydroxyurethanes **C** but also the abovementioned condensates **AB**, which are described in detail in U.S. Patent No.6,521,700 herein incorporated by reference. These condensation products **AB** of an acid-functional resin **A** and a hydroxyl-containing resin **B**, the resin **A**  
15 preferably having an acid number of from 100 to 230 mg/g, in particular from 120 to 160 mg/g, and a resin **B** preferably having a hydroxyl number from 50 to 500 mg/g, in particular from 60 to 350 mg/g, preferably have an acid number of from 25 to 75 mg/g, in particular from 30 to  
20 50 mg/g. Their Staudinger index ("intrinsic viscosity number", measured in dimethylformamide solvent at 23 °C) is normally from 10 to 20 cm<sup>3</sup> /g, in particular from 12 to 19 cm<sup>3</sup>/g, and especially preferred from 13 to 18 cm<sup>3</sup>/g.

25 The mass fraction of the hydroxy urethanes **C** in the sum of the masses of the condensation products **AB** and of the hydroxyurethane **C** is between 5 and 40 % (from 5 to 40 cg/g, the specified masses being in each case those of the solids fractions). The mass fraction of **C** is  
30 preferably from 10 to 35 cg/g, in particular from 15 to 30 cg/g.

In the preparation of the condensation product **AB**, components **A** and **B** are used preferably in a mass ratio of  
35 from 10:90 to 80:20, in particular from 15:85 to 40:60.

The condensation products **AB** are prepared from the polyhydroxy components **B** and the polyacyl components **A** under condensation conditions, i.e., at a temperature of from 80 to 180 °C, preferably between 90 and 170 °C,  
5 preferably in the presence of solvents which form azeotropes with the water formed during the condensation. The condensation is continued until the condensation products **AB** have the acid numbers specified above. Following at least partial neutralization of the  
10 remaining carboxyl groups (with preferably from 10 to 80 % of the carboxyl groups being neutralized, more preferably from 25 % to 70 %) the condensation products **AB** are dispersible in water. During the condensation it is possible to observe how the reaction mixture, which is  
15 cloudy to begin with, becomes clear and forms a homogeneous phase.

The resins **A** with acid groups are preferably selected from polyester resins **A1**, polyurethane resins **A2**, those known as maleate oils **A3**, the graft products **A4** of fatty acids and mixtures thereof grafted with unsaturated carboxylic acids, acrylic resins **A5**, and phosphoric or phosphonic-acid-modified epoxy resins **A6**. The acid number of the resins **A** is preferably from 100 to 230 mg/g, in particular from 70 to 160 mg/g. Their Staudinger index, measured in dimethylformamide solvent at 23 °C, is generally from about 6.5 to 12 cm<sup>3</sup>/g, preferably from 8 to 11 cm<sup>3</sup>/g.

30 Suitable polyester resins **A1** can be prepared conventionally from polyols **A11** and polycarboxylic acids **A12**, it being possible for some - preferably up to 25 % - of the amount of substance of the polyols and polycarboxylic acids to be replaced by hydroxycarboxylic acids  
35 **A13**. An appropriate choice of the nature and amount of

the reactants **A11** and **A12** ensures that the resultant polyester has a sufficient number of acid groups, corresponding to the acid number indicated above. The polyols **A11** are preferably selected from aliphatic and cycloaliphatic alcohols having 2 to 10 carbon atoms and on average at least two hydroxyl groups per molecule: those particularly suitable include glycol, 1,2- and 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene and triethylene glycol, dipropylene and tripolypropylene glycol, glycerol, trimethylolpropane, and trimethylolethane. Suitable polycarboxylic acids **A12** are aliphatic, cycloaliphatic, and aromatic polycarboxylic acids such as adipic acid, succinic acid, cyclohexanedicarboxylic acid, phthalic acid, isophthalic and terephthalic acid, trimellitic acid and trimesic acid, and benzophenonetetracarboxylic acid. It is also possible to use compounds which contain both carboxylic and sulfonic acid groups, such as sulfoisophthalic acid, for example.

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Suitable polyurethane resins **A2** can be prepared by reacting aliphatic polyols **A21** as defined under **A11**, hydroxyalkanecarboxylic acids **A22** having at least one, preferably two, hydroxyl groups and a carboxyl group which is less reactive than adipic acid under esterification conditions; preference is given to using dihydroxy monocarboxylic acids selected from dimethylolacetic acid, dimethylolbutyric acid, and dimethylolpropionic acid, oligomeric or polymeric compounds **A25** having on average at least two hydroxyl groups per molecule, which can be selected from polyetherpolyols **A251**, polyesterpolyols **A252**, polycarbonatepolyols **A253**, and saturated and unsaturated dihydroxyaliphatic compounds **A254**, which are obtainable by oligomerizing or polymerizing dienes having 4 to 12 carbon atoms, especially butadiene, isoprene, and

dimethylbutadiene, and then functionalizing them, in a known manner, and also polyfunctional isocyanates **A23**, preferably selected from aromatic, cycloaliphatic, and linear and branched aliphatic difunctional isocyanates 5 such as tolylene diisocyanate, bis(4-isocyanatophenyl)-methane, tetramethylxylylene diisocyanate, isophorone diisocyanate, bis(4-isocyanatocyclohexyl)methane, hexamethylene diisocyanate, and 1,6-diisocyanato-3,3,5- and -3,5,5-trimethylhexane.

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Particular preference is given to polyurethane resins **A2** preparable by reacting a mixture of one or more polyols **A21** with a hydroxyalkanecarboxylic acid **A22** and at least one polyfunctional isocyanate **A23** blocked at least partially, normally to more than 20 %, preferably to more than 35 %, and in particular to 50 % or more, with mono-hydroxy compounds **A24** selected from polyalkylene glycol monoalkyl ethers  $\text{HO-(R}^1\text{-O)}_n\text{-R}^2$ , where  $\text{R}^1$  is a linear or branched alkylene radical having 2 to 6, preferably 2 to 4, carbon atoms and  $\text{R}^2$  is an alkyl group having 1 to 8, preferably 2 to 6, carbon atoms and from oximes of aliphatic ketones having 3 to 9 carbon atoms and  $n$  is an integer of from 1 to 40. The degree of blocking is specified here as the fraction of the blocked isocyanate groups, based on the total (blocked and nonblocked) isocyanate groups present in the isocyanate **A23**. It is further preferred to prepare the polyurethane resins **A2** by reacting a mixture of a polyfunctional isocyanate and of a polyfunctional isocyanate blocked in the manner described above with the hydroxyalkanecarboxylic acid **A22** and the polyols **A21** and **A25**, the proportions of the mixture being such that in each molecule of the polyurethane **A2** there is on average one or more than one terminal blocked isocyanate group.

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"Maleate oils" **A3** are reaction products of (drying) oils **A31** and olefinically unsaturated carboxylic acids **A32**, especially dicarboxylic acids. The oils **A31** used are preferably drying and semidrying oils such as linseed oil, tall oil, rapeseed oil, sunflower oil, and cotton seed oil, with iodine numbers of from about 100 to about 180. The unsaturated carboxylic acids **A32** are selected such that under the customary conditions they undergo grafting free-radically (following the addition of initiators or after heating) to the initial charge of oils with a yield (fraction of unsaturated carboxylic acids joined to the oil after the reaction, based on the amount employed for the reaction) of more than 50 %. Among those particularly suitable are maleic acid in the form of its anhydride, and also tetrahydropthalic anhydride, acrylic and methacrylic acid, and citraconic, mesaconic, and itaconic acid.

Likewise suitable resins **A4** are fatty acids or mixtures thereof, **A41**, which have been grafted with the unsaturated acids specified under **A32**, the fatty acids or mixtures thereof being obtainable in industrial quantities by hydrolysis of fats. The fatty acids which are suitable have at least one olefinic double bond in their molecule: examples include oleic acid, linoleic and linolenic acid, ricinoleic acid, and elaidic acid, and also the said industrial mixtures of such acids.

Further suitable resins **A5** are the acidic acrylic resins which are obtainable by copolymerizing olefinically unsaturated carboxylic acids **A51** and other vinyl or acrylic monomers **A52**. The carboxylic acids are those already specified under **A32**, plus vinyl acetic acid and also crotonic and isocrotonic acid and the monoesters of olefinically unsaturated dicarboxylic acids such as monomethyl maleate and monomethyl fumarate, for example.

Suitable monomers **A52** are the alkyl esters of acrylic and methacrylic acid having preferably 1 to 8 carbon atoms in the alkyl group, (meth)acrylonitrile, hydroxylalkyl (meth)acrylates having 2 to 6 carbon atoms in the alkyl group, styrene, vinyltoluene, and vinyl esters of aliphatic linear and branched carboxylic acids having 2 to 15 carbon atoms, especially vinyl acetate and the vinyl ester of a mixture of branched aliphatic carboxylic acids having on average from 9 to 11 carbon atoms. It is also advantageous to copolymerize the monomers specified under **A51** and **A52** in the presence of compounds **A53** which react with the unsaturated carboxylic acids in an addition reaction with the formation of a carboxyl- or hydroxyl-functional copolymerizable compound. Examples of such compounds include lactones **A531**, which react with the carboxylic acids **A51** in a ring-opening reaction to form a carboxyl-functional unsaturated compound, and epoxides **A532**, especially glycidyl esters of  $\alpha$ -branched saturated aliphatic acids having 5 to 12 carbon atoms such as of neodecanoic acid or of neopentanoic acid, which react with the acid **A51** in an addition reaction to form a copolymerizable compound having one hydroxyl group. The amounts of substance of the compounds used are to be such that the required acid number is attained. If this compound **A53** is used as the initial charge and the polymerization is conducted in such a way that this compound is used as (sole) solvent, then solvent-free acrylic resins are obtained.

The phosphoric- or phosphonic-acid-modified epoxy resins or adducts of epoxy resins and fatty acids, **A6**, are prepared by reaction - preferably in a solvent - of phosphoric acid or of organic phosphonic acids which are at least dibasic with epoxy resins or with adducts of epoxy resins and fatty acids. The amount of substance of the phosphoric or phosphonic acid used is normally such

that all of the epoxide groups are consumed by the reaction of the acid and such that a sufficient number of acid groups is still available after the reaction. The resin formed contains hydroxyl groups (from the reaction of the oxirane group with the acid function) which are in a  $\beta$  position to the ester group; possibly hydroxyl groups in the glycidyl alcohol residues attached in the manner of ethers, from the epoxy resin; and acid groups of the phosphoric or phosphonic acid which were not consumed by the reaction with the epoxide.

Particularly suitable hydroxyl group-containing resins **B** are polyesters **B1**, acrylic resins **B2**, polyurethane resins **B3**, and epoxy resins **B4**. The hydroxyl number of the resins **B** is generally from about 50 to 500 mg/g, preferably from about 60 to 350 mg/g, and with particular preference from 70 to 300 mg/g. Their Staudinger index, measured at 23 °C and dimethylformamide solvent, is preferably from 8 to 13 cm<sup>3</sup>/g, and in particular from 9.5 to 12 cm<sup>3</sup>/g.

Like component **A1**, the polyesters **B1** are prepared by polycondensation; all that is necessary here is to choose the nature and amount of the reactants in such a way that there is an excess of hydroxyl groups over the acid groups, it being necessary for the condensation product to have the hydroxyl number specified above. This can be achieved by using polyhydric alcohols having on average at least two, preferably 2.1, hydroxyl groups per molecule with dicarboxylic acids or with a mixture of polycarboxylic and monocarboxylic acids having on average not more than two, preferably from 1.5 to 1.95, acid groups per molecule. Another possibility is to use a corresponding excess of hydroxyl components (polyols) **B11** over the acids **B12**. The polyols **B11** and the polyfunctional acids **B12** which are reacted in the

polycondensation reaction to give the hydroxyl-containing polyesters **B1** are selected from the same groups as the polyols **A11** and the acids **A12**. Here as well it is possible to replace some of the polyols and acids by 5 hydroxy acids in accordance with **A13**. The aim here is for the acid number of component **B** to be not above 20 mg/g, preferably below 18 mg/g. The acid number can be lowered, for example, by reacting the condensed polyester **B1** further with a small amount of monohydric aliphatic 10 alcohols **A14** under esterification conditions. In this reaction the amount of alcohols **A14** is to be calculated such that, although the acid number is lowered to below the limit, the Staudinger index does not fall below the stated lower limit. Examples of suitable aliphatic 15 alcohols include n-hexanol, 2-ethylhexanol, isodecyl alcohol, and tridecyl alcohol.

The hydroxyl group-containing acrylic resins **B2** are obtainable by normally free-radically initiated copolymerization of hydroxyl group-containing acrylic monomers **B21** with other vinyl or acrylic monomers **B22** without such functionality. Examples of the monomers **B21** are esters of acrylic and methacrylic acid with aliphatic polyols, especially diols having 2 to 10 carbon atoms, 20 such as hydroxyethyl and hydroxypropyl (meth)acrylate. Examples of the monomers **B22** are the alkyl esters of (meth)acrylic acid having 1 to 10 carbon atoms in the alkyl group such as methyl, ethyl, n-butyl, and 2-ethylhexyl (meth)acrylate, (meth)acrylonitrile, styrene, 25 vinyltoluene, and vinyl esters of aliphatic monocarboxylic acids having 1 to 10 carbon atoms such as vinyl acetate and vinyl propionate. Preference is also given to those acrylic resins not prepared in the usual manner in solution but instead in a bulk polymerization, 30 in which a liquid cyclic compound (see above, **A53**) is 35

introduced, which acts as a solvent during a polymerization reaction, and which during the reaction with one of the monomers used undergoes ring opening to form a copolymerizable compound. Examples of such compounds are  
5 glycidyl esters of  $\alpha$ -branched aliphatic monocarboxylic acids, especially the acids or acid mixtures available commercially as neopentanoic acid or neodecanoic acid, and also lactones such as  $\epsilon$ -caprolactone or  $\delta$ -valerolactone. If these glycidyl esters are used it is  
10 necessary in the polymerization to employ a fraction of acid-functional comonomers, such as (meth)acrylic acid, which is at least equimolar with the amount of substance of the epoxide groups. With ring opening, the lactones can be used with both hydroxyl group-containing and acid-  
15 functional comonomers.

Hydroxyl group-containing polyurethane resins **B3** are obtainable conventionally by addition reaction with oligomeric or polymeric polyols **B31**, selected from  
20 polyester polyols, polyether polyols, polycarbonate polyols, and polyolefin polyols, where appropriate, low molar mass aliphatic diols or polyols **B33** having 2 to 12 carbon atoms, such as ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, di-  
25 and tri-ethylene and -propylene glycol, neopentyl glycol, trimethylolpropane, and pentaerythritol, and polyfunctional isocyanates **B32**, the latter being used with a stoichiometric deficit such that the number of hydroxyl groups in the reaction mixture is greater than  
30 that of the isocyanate groups. Suitable polyols are, in particular, oligomeric and polymeric dihydroxy compounds having a number-average molar mass  $M_n$  of from about 200 to 10000 g/mol. By polyaddition with polyfunctional isocyanates, especially difunctional isocyanates, they  
35 are built up to the target value for the Staudinger index of at least 8 cm<sup>3</sup>/g, preferably at least 9.5 cm<sup>3</sup>/g.

Epoxy resins **B4**, which are obtainable by reacting a chlorohydrine with aliphatic or aromatic diols or polyols, especially bisphenol A, bisphenol F, recorcinol, novolaks or oligomeric polyoxyalkylene glycols having 2 to 4, preferably 3, carbon atoms in the alkylene group, contain one epoxide group per molecule of epichlorohydrin used. Instead of the reaction of epichlorohydrin with diols, the appropriate epoxy resins can also be prepared by the so-called advancement reaction from diglycidyl ethers of diols (such as those mentioned above) or diglycidyl esters of dibasic organic acids with said diols. All known epoxy resins can be used here, provided they satisfy the condition relating to the hydroxyl number.

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For crosslinking, the binder mixtures comprising the condensate **AB** and the admixture resin **C** are combined preferably with water-dilutable amino resins **D1**, especially melamine resins. It is, however, also possible where appropriate to use suitable blocked polyisocyanates **D2** as a curing component as well, in which case its proportion based on the mass of the curing agents used overall (in each case the fraction of the solids) can be preferably up to 30 % and with particular preference up 25 to 15 %. Admixing the hydroxyurethanes **C** considerably improves the stonechip resistance of the water-soluble binders thus modified, and the coatings produced therewith can be cured even at temperatures of from 130 to 140 °C. Surprisingly, the gloss as well is markedly improved.

30 The amino resin **D1** is preferably used in partly or fully etherified form. Particularly suitable are melamine resins such as hexamethoxymethylmelamine, products etherified with butanol or with mixtures of butanol and methanol, and also the corresponding benzoguanamine,

caprinoguanamine or acetoguanamine resins. Melamine resins are preferred, and may be partly or fully etherified, with methanol being the preferred etherifying alcohol.

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Suitable blocked isocyanates **D2** are obtainable by reacting polyfunctional aromatic, aliphatic or mixed aromatic-aliphatic isocyanates with monofunctional compounds which are reactive towards isocyanate and are referred to as blocking agents. The products of this reaction are cleaved back into their reactants, isocyanate and blocking agent, at elevated temperature, i.e., at above 100 °C, preferably at above just 100 °C, and in certain cases even from 80 °C upward. In the curing process the blocking agent is released and is able to escape from the coating film, which as yet is incompletely cured. Preference is given to blocked isocyanates which are obtainable conventionally from diisocyanates such as tolylene diisocyanate, isophorone diisocyanate, bis(4-isocyanatophenyl)methane, 1,6-diisocyanatohexane, tetramethylxylylene diisocyanate, and the allophanates, biurets, uretdiones formed from these diisocyanates, and customary blocking agents. Examples of such customary blocking agents are linear or branched aliphatic alcohols having 3 to 20 carbon atoms, preferably 2-ethylhexanol; phenols such as phenol itself; glycol monoesters, where the glycols can be monomeric or oligomeric alkylene glycols such as glycol itself, 1,2- and 1,3-propanediol, 1,4-butanediol, diethylene and triethylene glycol or dipropylene and tripropylene glycol, and the acid is selected from aliphatic monocarboxylic acids having 1 to 10 carbon atoms, preferably acetic acid; glycol monoethers, where the glycols are those mentioned above and the etherifying component is selected from lower aliphatic alcohols having 1 to 8 carbon atoms, preferably butyl glycol; or

ketoximes of aliphatic ketones having 3 to 10 carbon atoms, such as butanone oxime, for example. It is particularly preferred to use 3,5-dimethylpyrazole as a blocking agent, since it is not toxic and does not yellow even at temperatures of 180 °C or more. The blocking agents are normally chosen so that the unblocking temperature is between 80 and 180 °C. Particular preference is given to blocked isocyanates based on isophorone diisocyanate and 1,6-diisocyanatohexane.

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It is also possible to use hydrophilic blocked isocyanates. In this context, refer to the relevant disclosure content of Austrian patent AT-B 408 657, which is incorporated herein by reference.

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The invention further provides aqueous coating materials which comprise the condensation products **AB**, the hydroxy-urethanes **C** and curing agents **D**, and also pigments and fillers plus, if desired, further additives such as wetting agents, antisettling agents, flow improvers, thickeners, and leveling agents.

With the aqueous binders of the invention it is possible to formulate aqueous coating materials which lead to coatings having high gloss and good resistance to stonechipping. Such coating materials are employed in particular for automotive surfacers. The coating materials are preferably prepared by mixing components **AB** and **C**, dividing this mixture, the first portion being intimately mixed with pigments and fillers and other additives to form a paste and subsequently formulating this paste to the finished coating material by adding the remainder of the mixture of **AB** and **C**, the curing agent **D**, and, where appropriate, further additives and water.

35

The examples below illustrate the invention.

**Examples**

In the examples below, as in the foregoing text, all figures with the unit "%" denote mass fractions (ratio of the mass of the substance in question to the mass of the mixture), unless specified otherwise. Concentration figures in "%" are mass fractions of the dissolved substance in the solution (mass of the dissolved substance divided by the mass of the solution). In the examples the following abbreviations have been used (M: molar mass):

EP380	diepoxy resin having a specific epoxide group content of about 5.26 mol/kg ("epoxide equivalent weight" EEW about 190 g/mol)	
DGM	diethylene glycol dimethyl ether	
MIBK	methyl isobutyl ketone	
TDI	tolylene diisocyanate	M = 174 g/mol
HD	1,6-hexanediol	M = 118 g/mol
20 BD	1,4-butanediol	M = 90 g/mol
CD	polycaprolactonediol*	M = 550 g/mol
DEG	diethylene glycol	M = 106 g/mol
TPG	tripropylene glycol	M = 192 g/mol
DPG	dipropylene glycol	M = 134 g/mol
25 TMP	trimethylolpropane	M = 134 g/mol
IPDI	isophorone diisocyanate	M = 222 g/mol
DCHDI	dicyclohexylmethane diisocyanate	M = 262 g/mol
TMXDI	tetramethylxylylene diisocyanate	M = 244 g/mol
30 THDI	trimerized hexamethylene diisocyanate+	M = 575 g/mol

\* ®Placcel 205, Interorgana

35 + Desmodur N 3300, Bayer

**Preparation of admixture component C:**

C1: A three-necked flask equipped with stirrer and reflux condenser was charged with 236 g (2.0 mol) of 1,6-hexanediol and 90 g (1.0 mol) of 1,4-butanediol and the mixture was heated to 80 °C. Subsequently 444 g (2.0 mol) of isophorone diisocyanate were added over the course of two hours with stirring. With occasional cooling the temperature was allowed to rise to 90 °C. When addition was complete the reaction mixture was held at 90 °C until free isocyanate was no longer detectable (about 2 h). Finally, the product was diluted with methoxypropanol to a mass fraction of solids of about 80 % (NVC, nonvolatiles content). This gave a product having a Staudinger index ("intrinsic viscosity number", measured in dimethylformamide at 23 °C) of 5.5 cm<sup>3</sup>/g.

20 In analogy to the procedure described above, further dihydroxyurethanes were prepared (see Table 1).

Table 1 Preparation of dihydroxyurethanes

<b>Admixture resin</b>	<b>Dihydroxy compound type <math>n_h</math> in mol <math>m_h</math> in g</b>	<b>Diisocyanate type <math>n_i</math> in mol <math>m_i</math> in g</b>	<b>Staudinger index <math>J_0</math> in cm<sup>3</sup>/g</b>	<b>Yield resin solids <math>m_s</math> in g</b>	<b>Hydroxyl number in mg/g</b>
C1	HD 2.0 236 BD 1.0 90	IPDI 2.0 444	5.5	770	145
C2	BD 2.0 180 CD 1.0 550	DCHDI 2.2 576	8.9	1306	69
C3	DEG 2.0 212 CD 0.5 275	DCHDI 1.5 393	4.8	880	127
C4	HD 2.2 260 TPG 0.8 154	IPDI 2.0 444	6.7	858	130
C5	BD 2.0 180 CD 1.0 550	TMXDI 2.1 512	6.8	1242	81
C6	BD 3.3 297 CD 0.7 385	IPDI 3.0 666	7.8	1348	83
C7	HD 2.0 236 DPG 1.0 134	IPDI 1.0 222 TMXDI 1.0 244	6.4	836	134
C8	TMP 2.0 268 CD 0.5 275 BD 0.5 45	IPDI 2.0 444	7	1032	108
C9	HD 2.0 236 BD 1.0 90	IPDI 2.0 444 THDI 0.1 57	8	827	122

- n<sub>H</sub>; m<sub>H</sub>:** Amount of substance and mass of hydroxy compound **C<sub>a</sub>**
- n<sub>I</sub>; m<sub>I</sub>:** Amount of substance and mass of isocyanate compound **C<sub>b</sub>**
- 5   **m<sub>s</sub>:** Mass of resin solids of hydroxyurethane **C**

**Polyester PE (comparative example)**

10   A three-necked flask equipped with stirrer and reflux condenser was charged with 150 g (1.0 mol) of triethylene glycol and this initial charge was heated to 120 °C under inert gas. Then 148 g (1.0 mol) phthalic anhydride were added and the temperature was raised to 150 °C, utilizing  
15   the heat given off. When an acid number of 180 mg/g had been reached 134 g (1.0 mol) of trimethylolpropane were added, the batch was slowly heated to 220 °C, a distillation circuit was set up with xylene, and, with removal of the water of reaction produced, esterification  
20   was carried out until an acid number of less than 5 mg/g was reached. Finally the azeotrope former was stripped off by distillation under reduced pressure.

**Preparation of the polycarboxyl components A**

25

**Carboxyl-containing polyurethane (A 1)**

A suitable reaction vessel was charged with a solution of 810 g (6 mol) of dimethylolpropionic acid in 946 g of DGM  
30   and 526 g of MIBK. Over the course of 4 hours a mixture of 870 g (5 mol) of TDI and 528 g (2 mol) of TDI semiblocked with ethylene glycol monoethyl ether simultaneously was added to this solution at 100 °C. As soon as all the NCO groups had reacted the batch was  
35   diluted with a mixture of DGM and MIBK (mass ratio 2:1) to a mass fraction of solids of 60 %. The component (A1)

had an acid number of 140 mg/g and a Staudinger index ("intrinsic viscosity number"), measured in N,N-dimethylformamide (DMF) at 23 °C, of 9.3 cm<sup>3</sup>/g.

- 5 The semiblocked TDI was prepared by adding 90 g (1 mol) of ethylene glycol monoethyl ether to 174 g (1 mol) of TDI over the course of 2 hours at 30 °C and then reacting the mixture until it had a mass fraction of unreacted isocyanate groups ("NCO value") of 16 to 17 %.

10

#### **Acid-modified epoxy resin (A 2)**

An appropriate reaction vessel was charged with a mixture of 146 g (1.0 mol) of adipic acid, 40 g (0.3 mol) of phosphoric acid (75 % strength solution in water) and 46 g of methoxypropanol. The mixture was heated to 70 °C and over the course of 1 hour 323 g (amount of substance of epoxide groups 1.7 mol) of EP 380 were added with stirring. As a result of the slight exotherm the temperature rose to about 80 °C. When addition was complete the batch was heated to 110 °C and held at this temperature until an acid number of 130 to 140 mg/g was reached.

25 **Carboxyl-containing polyester (A 3)**

A three-necked flask equipped with stirrer and reflux condenser was charged with 140 g (1.3 mol) of diethylene glycol and 152 g (1.1 mol) of trimethylolpropane. With stirring and under inert gas the mixture was heated to 100 °C and at this temperature, in portions, 109 g (0.6 mol) of isophthalic acid, 96 g (0.6 mol) of adipic acid and lastly 198 g (1.3 mol) of phthalic anhydride were added. The temperature was raised to 130 °C, utilizing the heat evolved during the reaction.

After the batch had been held at 130 °C for two hours it was slowly heated to 180 °C and esterified, with removal of the water of reaction which was now produced, to an acid number of 50 mg/g.

5

When the stated acid number had been reached the product was diluted with butyl glycol to a mass fraction of solids of 60 % and finally was neutralized by adding 14 g (0.16 mol) of N,N-dimethylethanolamine.

10

The product thus obtained was infinitely water-dilutable.

#### **Preparation of polyhydroxyl components B**

15    **Polyester (B 1):**

In a suitable reaction vessel 130 g (1.1 mol) of hexane-1,6-diol, 82 g (0.6 mol) of pentaerythritol, 8 g (0.05 mol) of isononanoic acid, 28 g (0.1 mol) of 20 ricinene fatty acid (dehydrated castor oil fatty acid) and 50 g (0.3 mol) of isophthalic acid were esterified at 210 °C to an acid number of less than 4 mg/g. The viscosity of a 50 % strength solution in ethylene glycol monobutyl ether, measured as the efflux time in accordance with DIN 53211 at 20 °C, was 125 seconds and the Staudinger index, measured in N,N-dimethylformamide at 23 °C, was 9.8 cm<sup>3</sup>/g.

#### **Polyester (B 2):**

30

In the same way as for polyester B 1, 38 g (0.2 mol) of tripropylene glycol, 125 g (1.2 mol) of neopentyl glycol, 28 g (0.1 mol) of isomerized linoleic acid, 83 g (0.5 mol) of isophthalic acid and 58 g (0.3 mol) of 35 trimellitic anhydride were esterified at 230 °C to an acid number of less than 4 mg/g. The viscosity of a 50 %

strength solution in ethylene glycol monobutyl ether, measured as the efflux time in accordance with DIN 53211 at 20 °C, was 165 seconds. The Staudinger index, measured in N,N-dimethylformamide at 23 °C, was 10.5 cm<sup>3</sup>/g.

5

**Preparation of binder components (condensation products AB)**

In accordance with the mass ratios indicated in Table 2  
10 the polycarboxyl components (A) and the polyhydroxyl components (B) were mixed and the solvent present was largely removed under reduced pressure while heating to a reaction temperature of 160 °C. This temperature was maintained until the desired acid number had been  
15 reached, at which point a sample was perfectly dilutable with water following neutralization with dimethylethanolamine. 80 g of the condensate (solids) obtained in this way were mixed at 90 °C with in each case 20 g (solids) of the stated dihydroxyurethane C,  
20 neutralized with the corresponding amount of dimethylethanolamine to a degree of neutralization of 80 % (based on the acid groups present in each case), and, after a homogenizing time of 30 minutes, diluted  
25 with water in portions to a viscosity of below 3000 mPa·s at 23 °C.

In the case of the comparative examples the compound mixed in was, instead of the dihydroxyurethane, 20 g (solids) of a low molar mass, hydroxyl group-containing  
30 polyester (PE).

In the case of the control sample the condensate formed from the polycarboxyl component (A) and the polyhydroxyl component (B) was neutralized as indicated above, without  
35 further modification, and diluted with water.

Table 2

Example	Component A	Component B	Acid number of condensate AB	Admixture component C	Viscosity (23 °C)	Mass fraction of solids in %
	Mass type in g	Mass type in g	mg/g	Mass type in g	η in mPa·s	
1	30 A1	50 B1	45	20 C1	2607	46
2	30 A2	50 B2	43	20 C2	2433	39.4
3	30 A1	50 B1	43	20 C3	2130	41
4	30 A1	50 B1	42	20 C4	2233	38.8
5	30 A2	50 B2	42	20 C5	1980	44.2
6	30 A2	50 B2	44	20 C6	2330	42
7	30 A1	50 B1	43	20 C7	1844	41.2
8	30 A2	50 B2	47	20 C8	2720	38.6
9	30 A3		50	20 C9	1977	37.8
10	30 A3		50	20 C1	1739	40.9
<b>Comparative examples</b>						
11	30 A1	50 B1	43	20 PE	2226	37
12	30 A2	50 B2	42	20 PE	1989	37.8
13	30 A3		50	20 PE	2243	36.2
15						

**Performance testing:**

Testing of the binders of the invention as automotive surfacers

5

Using the formulations indicated in Table 3, aqueous surfacer materials were prepared by a customary procedure and were each adjusted to a viscosity of 120 mPa·s (1.2 poise) by further addition of deionized water  
10 (designated in the table by "deionized water 2"). Coating paints 1 to 5 were applied to cleaned glass plates using a 150 µm doctor blade and after a 15-minute flash-off period were baked at 140 °C for 20 minutes. The coatings obtained were used for determination of the pendulum  
15 hardness and the gloss, and were also subjected to visual assessment.

Table 3: Surfacer examples

			Paint 1	Paint 2	Paint 3	Paint 4	Paint 5
5	Binder 1	in g	91.8	-	-	-	-
	Binder 3	in g	-	103.0	-	-	-
	Binder 8	in g	-	-	109.2	-	-
	Binder 11 (comparative)	in g	-	-	-	114.0	-
10	Binder 12 (comparative)	in g	-	-	-	-	111.6
	Wetting agent*	in g	1.2	1.2	1.2	1.2	1.2
	Deionized water 1	in g	15.0	18.0	25.0	28.0	25.0
	Titanium dioxide	in g	60.0	60.0	60.0	60.0	60.0
15	Filler	in g	60.0	60.0	60.0	60.0	60.0
	Binder 1	in g	130.0	-	-	-	-
	Binder 3	in g	-	145.8	-	-	-
	Binder 8	in g	-	-	155.2	-	-
	Binder 11 (comparative)	in g	-	-	-	161.6	-
	Binder 12 (comparative)	in g	-	-	-	-	158.2
	Amino resin†	in g	18.0	18.0	18.0	18.0	18.0
	Deionized water 2	in g	6	9.0	18.0	20.0	17

	<b>Paint 1</b>	<b>Paint 2</b>	<b>Paint 3</b>	<b>Paint 4</b>	<b>Paint 5</b>
Mass of paint in g	382.0	415.0	446.6	462.8	451.0
Appearance of cured paint film	defect free	defect free	defect free	defect free	defect free
Dry film thickness in µm	37	35	34	33	34
Pendulum hardness	115	103	132	45	53
gloss(measured at an angle of 60°)	91	90	90	85	86

Pendulum hardness: Pendulum hardness according to König (DIN 53157) measured after baking (20 minutes at 140 °C) and 1 hour of storage under standard conditions

- 5 \*Wetting agent is ®Surfynol 104E (Air Products)  
+Filler is barium sulfate (®Blanc fixe super F,  
Sachtleben)  
‡ ® Maprenal MF 904, Solutia Germany GmbH & Co. KG

10 Result:

All paints produced defect-free film surfacers; the gloss of paints 1, 2, and 3 (based on the inventive binders) is significantly higher than that of the comparative paints (paints 4 and 5). The film hardness of the coatings based 15 on inventive binders (paints 1, 2, and 3) corresponds to the requirements imposed on aqueous automotive surfacers, whereas the film hardness of the comparative paints is clearly too low.

20 Metal test panels for the stonechip test:

Test system: Bonder 26 60 OC as substrate, 25 µm of a standard electrocoat primer, 35 µm of the aqueous surfacer of paints 1 to 5, 40 µm of a standard commercial acrylic-melamine topcoat.

25

Baking conditions for  
the electrocoat primer: 30 minutes at 175 °C

Baking conditions for  
surfacers (paints 1 to 5): 20 minutes at 140 °C

30 Baking conditions for  
topcoat: 30 minutes at 140 °C

After the test panels prepared in this way had been baked they were stored under standard conditions for 24 hours 35 and then subjected to a stonechip test in accordance with

DIN standard 55996-1 (2 passes each with 0.5 kg of angular shot material, pressure: 2 bar)

- 5      Test panel 1:                    electrocoat primer, surfacer based on paint 1, topcoat
- Test panel 2:                    electrocoat primer, surfacer based on paint 2, topcoat
- Test panel 3:                    electrocoat primer, surfacer based on paint 3, topcoat
- 10     Test panel 4  
(comparative):                    electrocoat primer, surfacer based on paint 4, topcoat
- Test panel 5  
(comparative):                    electrocoat primer, surfacer based on paint 5, topcoat
- 15

Result:

20     The stonechip indices compiled in Table 4 show that with the binders according to the invention outstanding results were obtained, while the comparisons without the addition of the hydroxyurethanes as an admixture resin give inadequate results in the stonechip test.

25

Table 4   Results of the stonechip test

	Stonechip index according to DIN standard 55996-1
30	Test panel 1                    0 to 1
	Test panel 2                    1 to 2
	Test panel 3                    1 to 2
	Test panel 4                    4 to 5
	Test panel 5                    4